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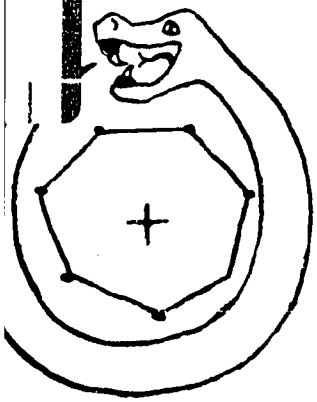
ABSTRACT

This booklet, one of a series of 17 developed at Prince George's Community College, Largo, Maryland, provides an individualized, self-paced undergraduate organic chemistry instruction module designed to augment any course in organic chemistry but particularly those taught using the text "Organic Chemistry" by Morrison and Boyd. The entire series of modules covers the first 13 chapters of the Morrison-Boyd text in great detail. Each module has been provided with from one to three audiotapes, available from Prince George's Community College, to provide students additional explanations of particular concepts. Each module includes a self-evaluation exercise, a reference guide, worksheets to be completed with the audiotapes, answer sheets for the worksheets, a progress evaluation, an answer sheet for the progress evaluation, an answer sheet for the self-evaluation exercise, an introduction to the topic covered by the module, and student performance objectives for the module. The topic of this module is benzene-aromaticity. (SL)

ORGANIC CHEMISTRY



7 BONDS

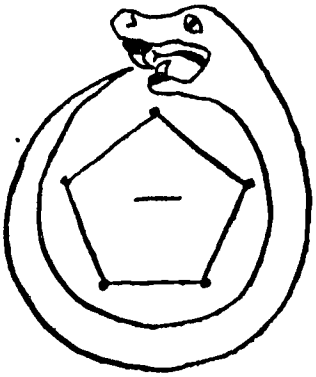
V. Zdravkovich

15

Self

Instructional

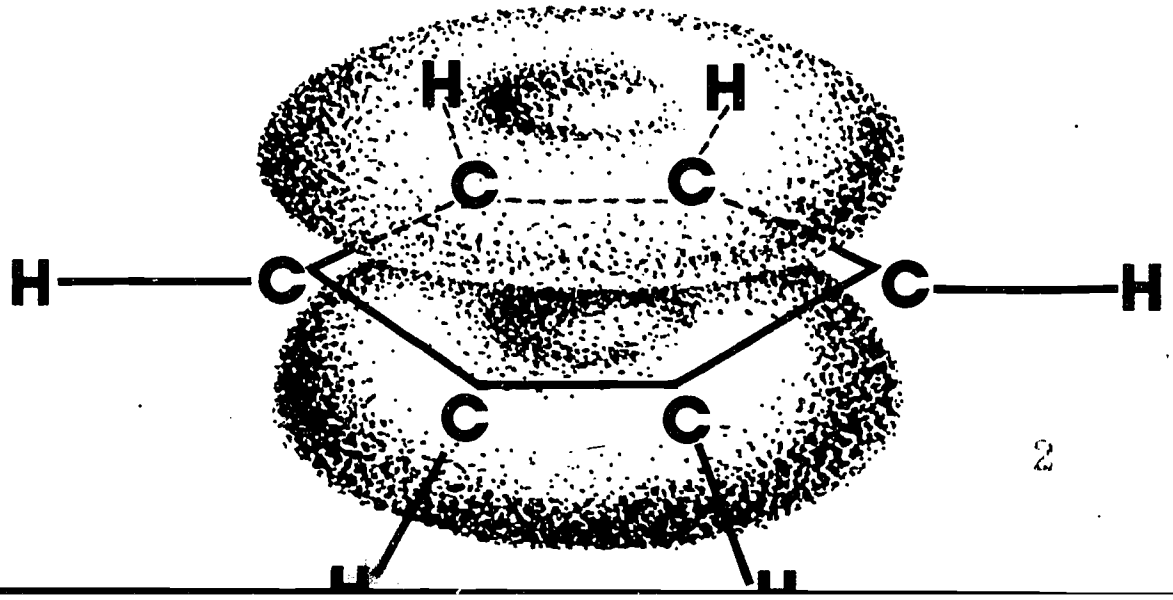
Package



5 BONDS

BENZENE, AROMATICITY

6 BONDS NEUTRAL



Self Instructional Sequence in

ORGANIC CHEMISTRY

BENZENE-AROMATICITY

In this self instructional package you will cross the thresholds of a fascinating field of aromatic chemistry. Like Alice in Wonderland you will gain new acquaintances. In your case these new acquaintances will be: compounds, reactions, mechanisms, concepts. We would never have heard about Alice, Queen of Hearts, The Mad Hatter and The Cheshire cat had it not been for Lewis Carol. In a similar manner, the exciting field of aromatic chemistry would have remained unknown for a longer period of time had it not been for a fascinating man called August Friedrich Kekule. Kekule was originally a student of architecture who was won over to chemistry by Professor Liebig's lectures. After his graduation he slowly fought his way to success and international fame. Wohler is known as the father of organic chemistry, but Kekule was really the best promoter of organic chemistry. At a time when laboratory equipment was below the level of the chemistry kit you can buy in any toy store today, he presented a paper in which he recognized carbon as a tetravolent element. He began the first textbook of organic chemistry (3 volumes, 2165 pages, published in 1861-1862), invented atomic models and eighty years ahead of his time, in 1865, he proposed the correct structure of benzene. He thus opened the door to the aromatic wonderland.

He stepped through the looking glass like Alice and he made reality out of a dream by completing the "benzol" picture. (The term in English and American literature is benzene) Here is his own account of the dream:

> *There I sat and wrote my Lehrbuch, but it did not proceed well, my mind was elsewhere. I turned the chair to the fireplace and fell half asleep. Again the atoms gamboled before my eyes. Smaller groups this time kept modestly to the background. My mind's eyes, trained by repeated visions of a similar kind, now distinguished larger formations of various shapes. Long rows, in many ways more densely joined; everything in movement, winding and turning like snakes. And look, what was that? One snake grabbed its own tail, and mockingly the shape whirled before my eyes. As if struck by lightning I awoke; this time again I spent the rest of the night to work out the consequences.*

BENZENE-AROMATICITY

Definitions

The student will be able to define and illustrate with appropriate examples where applicable the following terms: Kekule formula, Resonance stabilization energy, Delocalization energy, ORTHO, META AND PARA positions in benzene.

Nomenclature

The student will be able to assign the correct IUPAC names to different monosubstituted, disubstituted and trisubstituted derivatives of benzene.

The student will be able to draw the structural formula which corresponds to the given IUPAC name.

Reaction Mechanisms

The student will be able to write the step by step mechanism for the following reactions: Nitration, sulfonation, Protodesulfonation, Friedel-Crafts alkylation and acylation reaction, halogenation.

The student will be able to write the step by step mechanism for the electrophilic aromatic substitution in general.

The student will be able to write the resonance structures showing the stabilization of the intermediate carbonium ion.

The student will be able to identify the rate determining step in the mechanism and to explain it on the basis of the isotope effect.

Reactions

The student will be able to identify the reactants, reagents and the products in the following reactions: nitration, sulfonation, Friedel-Crafts alkylation and acetylation, Clemensen reduction, protodesulfonation, thallation, halogenation, hydrogenation and the oxidation of an arene.

The student will be able to identify the reagents required for the synthesis of different products.

BENZENE-AROMATICITY

Identify statements below as True or False by placing a capital T or F in the space to the left.

1. _____ Resonance Stabilization Energy is the energy liberated when the resonance structures are formed.

2. _____ The positive charge in the intermediate carbonium ion in an electrophilic aromatic substitution is delocalized over the remaining five carbon atoms.

3. _____ Addition of one mole of hydrogen to benzene results in the formation of a more stable species.

4. _____ Delocalization energy is energy liberated when the positive charge is delocalized over the ring.

5. _____ A majority of electrophilic aromatic substitution reactions show a prominent isotope effect.

6. _____ Resonance structures which illustrate the stabilization of the carbonium ion in an aromatic substitution show the positive charge to be located in o and p positions relative to the incoming group.

7. _____ Reaction of benzene with $CH_3\overset{O}{\overset{\|}{C}}-Cl$ in presence of $AlCl_3$ yields $C_6H_5-\overset{O}{\overset{\|}{C}}-CH_3$

8. _____ When p-methyl phenyl thalliumdifluoroacetate is heated to 75° a m-methyl phenylthalliumdifluoroacetate is obtained.

9. _____ Thallation is a highly regiospecific reaction.

Blacken out the correct answer or answers in the questions below.

10. The facts that illustrate the unusual stability of benzene ring are:

    a) there are three disubstituted derivatives of benzene

    b) benzene undergoes primarily substitution reactions

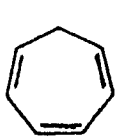
    c) heat of hydrogenation of benzene is lower than expected

    d) there is only one monosubstituted derivative of benzene

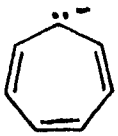
11. The requirements for the aromatic character are:

a) the number π electrons must be 4n+2.
b) a compound must possess cyclic structure.
c) a compound must possess a closed cloud of π electron density.
d) a compound must contain 4n+2 carbon atoms

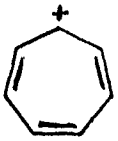
12. Of the compounds below the one or the ones that possess aromatic character is, are:



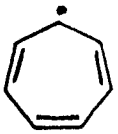
I
1,3,5-cyclo-heptatriene



II
1,3,5-cyclo-heptatrienyl anion

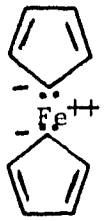


III
1,3,5-cyclo-heptatrienyl cation



IV
1,3,5-cyclo-heptatriene radical

a) I
b) II
c) III
d) IV

13. The existence of stable ferrocene  indicates that:

a) cyclopentadiene is a very stable species.
b) cyclopentadienyl anion is a very stable species.
c) cyclopentadiene is probably aromatic.
d) cyclopentadienyl anion is probably aromatic.

14. An aromatic compound has the following characteristic features:

a) it undergoes primarily addition reactions.
b) it demonstrates unusual stability.
c) all the carbon-carbon bonds in an aromatic compound are the same.
d) its heat of combustion is lower than expected.

15. The following features are characteristic for a proto desulfonation reaction:

a) it is the exact reverse of the sulfonation reaction.
b) the attacking species is proton or H^+.
c) the reactant is benzenesulfonic acid.
d) the reagent is concentrated sulfuric acid.

16. The attaching species in the sulfonation reaction is:

a) SO_3H^+

b) SO_3

c) SO_3^+

d) HSO_4^-

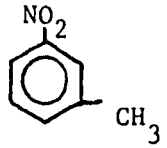
17. Ethylbenzene can be obtained in a reaction of benzene with:

a) ethanol and acid.
b) ethylchloride and hydrogenfluoride.

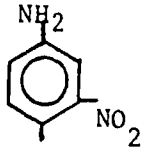
c) $CH_3-C(=O)-Cl$, $AlCl_3$, $Zn(H_g)$ acid,

d) ethylene and acid.

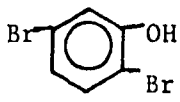
18. The correct IUPAC name for the compound below is:



a) m-methyl nitrobenzene
b) m-nitro toluene
c) 1-nitro-3-methyl benzene
d) O-nitro toluene

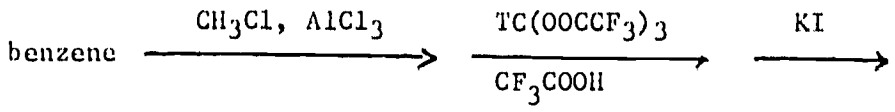
19. The correct name for  is:

a) 3-nitro-4-isopropyl phenol
b) 2-isopropyl-5-amino nitrobenzene
c) 1-amino-3-nitro-4-isopropyl benzene
d) 3-nitro-4-isopropyl aniline

20. The correct name for 

a) 2,5-dibromo aniline
b) 3,6-dibromophenol
c) 2,5-dibromophenol
d) 1-hydroxy-2,5-dibromo benzene

21. The compound obtained in the reaction sequence below is:



a) toluene
b) p-methyl phenyl thallium trifluoroacetate
c) p-iodotoluene
d) m-iodo methyl benzene

22. The reagents required for synthesis of benzoic acid from benzene is/are:

a) hot KM_nO_4
b) CH_3Cl, $AlCl_3$, hot KM_nO_4
c) HNO_3, hot KM_nO_4
d) NaOH

23. The reagents required for synthesis of n-propyl benzene from benzene are:

a) n-propyl alcohol, acid
b) $CH_3\ CH_2\ C(=O)Cl$, $AlCl_3$, $Zn(H_g)$ acid
c) n-propylchloride, BF_3
d) 1-propene, acid

24. The correct statements about an electrophilic aromatic substitution in general are:

a) they show a considerable isotope effect.
b) they are reversible.
c) the rate determining step is the formation of the carbonium ion.
d) the step which involves the dissociation of hydrogen positive ion has low energy of activation.

Self Instructional Package No. 15
Form C - Reference Guide

BENZENE-AROMATICITY

The Reference Guide should be used in conjunction with Form B or the Self Evaluation Exercise. The references give correlation between the questions in Form B and the available material in the textbook and in form of tapes.

Question 1	Chapter 10, Section 7	Morrison & Boyd
Question 2, 5, 6, 24	Chapter 11, Sections 8, 14, 15, 16, 17	Organic Chemistry
Question 3	Chapter 10, Section 5	
Question 4	Chapter 10, Section 8	
Question 7	Chapter 12, Section 5	
Questions 8, 9	Chapter 11, Section 13	
Question 10	Chapter 10, Sections 4, 5, 6	
Questions 11,12,13,14	Chapter 10, Section 10	
Question 15	Chapter 11, Section 12	
Question 16	Chapter 11, Section 9	
Questions 17, 23	Chapter 11, Sections 1, 10 Chapter 12, Section 7	
Questions 18, 19, 20	Chapter 10, Section 11	
Question 21	Chapter 11, Section 1,10,13 Chapter 12, Section 5	
Question 22	Chapter 11, Section 10 Chapter 12, Sections 9, 10	

For Questions 1,3,4,10,11,12,13,14 additional explanations and examples are provided in Tape 1 - Benzene-Aromaticity

For Questions 18,19,20 additional explanations and examples are provided in Tape 2 - Nomenclature

For Questions 2,5 : ,8,9,15,16,17,21,22,23,24 additional explanations and examples are provided in Tape 3 - Electrophilic Aromatic Substitution

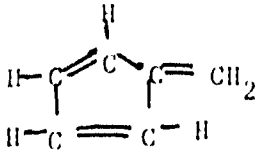
In dreams the exile cometh home;
In dreams the lost is found;
In dreams the captive's feet may roam. The world around.
---William Watson

BENZENE - AROMATICITY

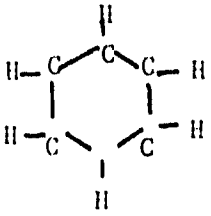
Example No. 1

Fact No. 1: The molecular formula of benzene is C_6H_6.

Possible structural formulas for benzene that correspond to C_6H_6 are:

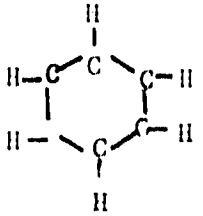


I

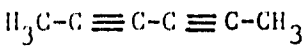


II

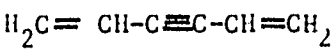
(Kekule formula)



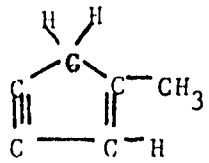
III



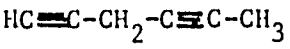
IV



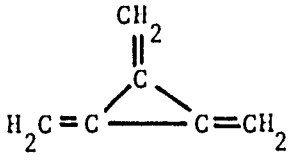
V



VI



VII



VIII

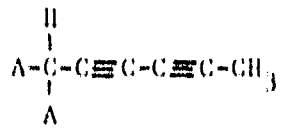
Fact No. 2: Benzene yields only one monosubstituted derivative C_6H_5A

Result: Structural formulas I, III, V, VI, and VII are eliminated.

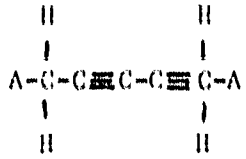
SIP No. 15
Tape 1 - Work Sheet

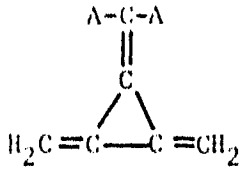
Fact No. 3: Benzene yields three disubstitution products $C_6H_4A_2$ or C_6H_4AB.

Result: Structural formulas IV and VIII is eliminated, because each can yield only two disubstituted derivatives:



and





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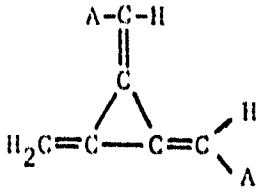
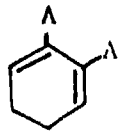
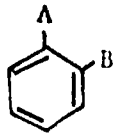


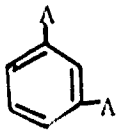
Example No. 2 - disubstituted derivatives of benzene

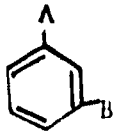


or

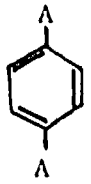


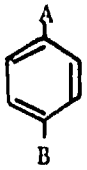
1,2-disubstituted derivative





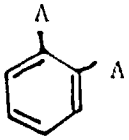
1,3-disubstituted derivative



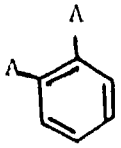


1,4-disubstituted derivative

Example No. 3



I

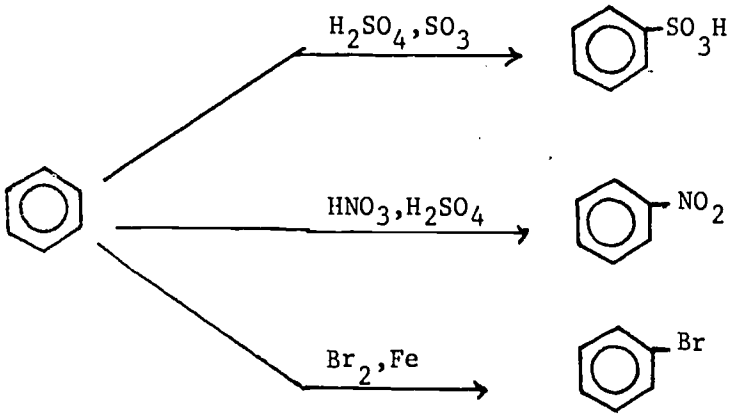


II

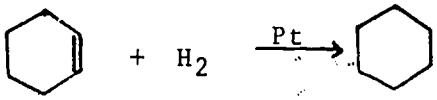
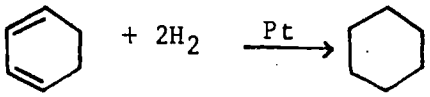
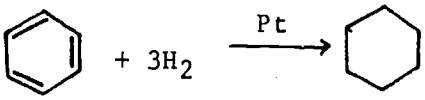
Example No. 4 - Kekule formula of benzene

Example No. 5 - Facts illustrating the unusual stability of benzene ring.

I. Benzene undergoes substitution rather than addition.

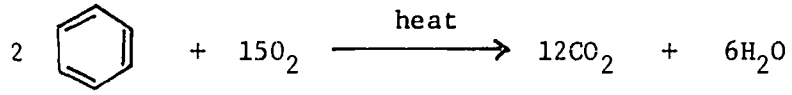


II. Heats of a) hydrogenation and b) combustion are considerably lower than expected.

a) Heat of hydrogenation - compound	Expected heat of hydrogenation (kcal/mole)	Observed heat of hydrogenation (kcal/mole)	Stabilization Energy (kcal/mole)
	28.6	28.6	---
	2 X 28.6 = 57.2	55.4	1.8
	3 X 28.6 = 85.8	49.8	36

Example No. 5 (continued)

II. b) Heat of combustion for benzene:



expected: 824.1 kcal/mole

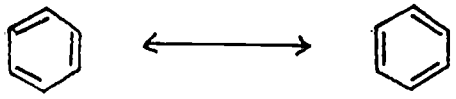
observed: 789.1 kcal/mole

stabilization energy: 35 kcal/mole

III. All carbon-carbon bonds in benzene are equal. Their length is intermediate between a single and a double bond.

Type of Bond	Length [Å]
carbon-carbon single bond	1.5
carbon-carbon double bond	1.34
carbon-carbon bond in benzene	1.39

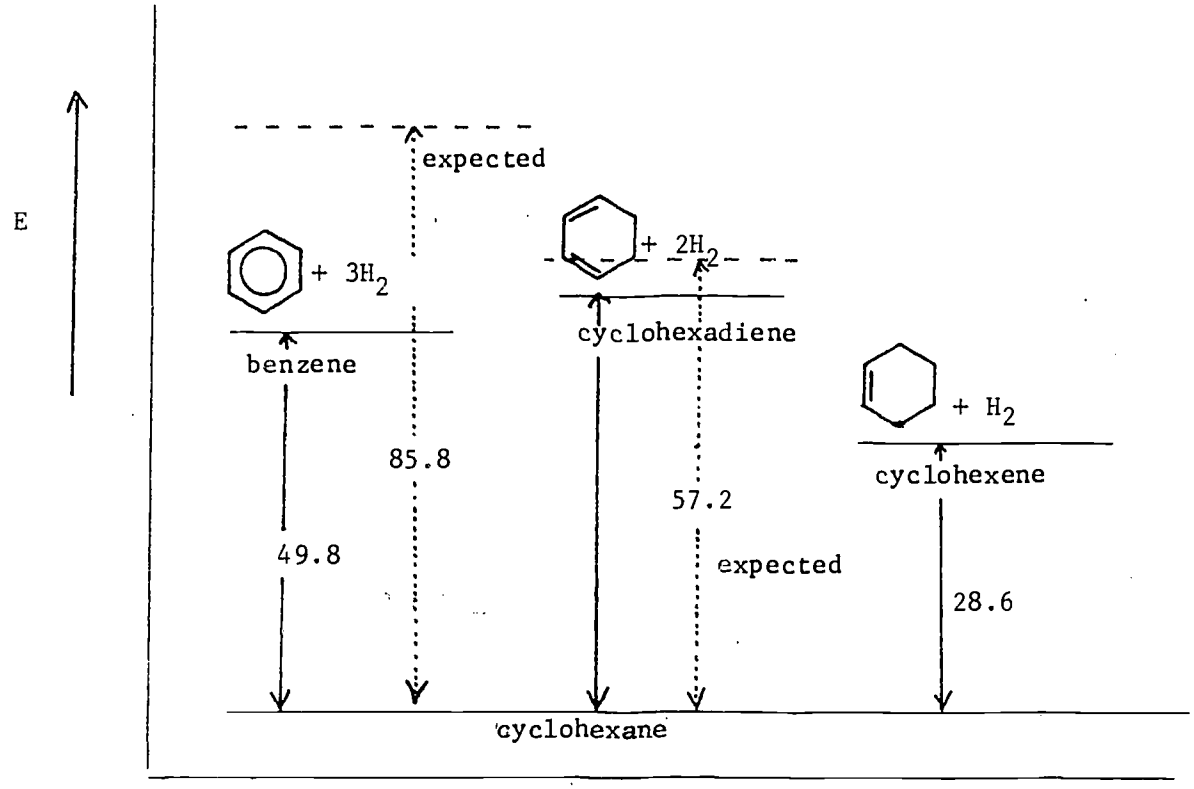
Example No. 6 - Resonance Theory



Resonance structures of benzene

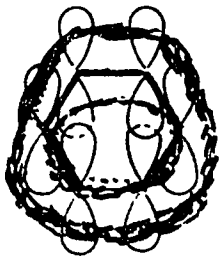
The actual formula of benzene is the resonance hybrid of I and II.

Example No. 7 - Relative stability of cyclohexane, cyclohexene, cyclohexadiene and benzene



Heats of hydrogenation and stability

Example No. 8 - Orbital picture of benzene



SIP No. 15
Tape 1 - Work Sheet

Example No. 9 - Aromaticity

Features characteristic for aromaticity are:

a) cyclic - ring structure

b) closed cloud of electron density

c) the number of π electrons must be equal to 4 n + 2 when n = 0,1,2,3, etc.

(when n = 0 4 x 0 + 2 = 2

when n = 1 4 x 1 + 2 = 6

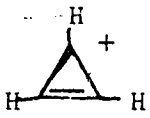
when n = 2 4 x 2 + 2 = 10)

The No. of π electrons should be 2 or 6 or 10 or 14 or 18 and so on.

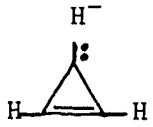
d) the compound will show resistance toward addition reactions in spite of a high degree of unsaturation.

e) the shape of the molecule is flat-planar with identical bond angles and carbon-carbon bond length.

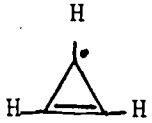
Example No. 10 - Identification of the aromatic character.



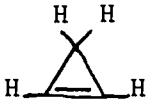
cyclopropylium cation



cyclopropylium anion



cyclopropene free radical



cyclopropene

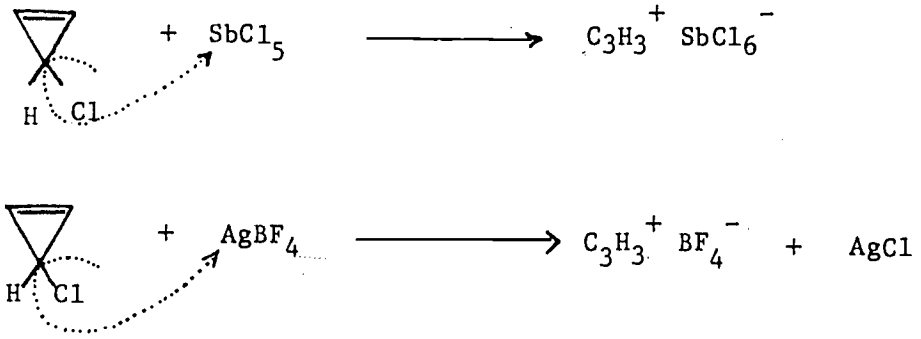
No. of π electrons: _____ _____ _____ _____

_____ possesses the necessary features and should be aromatic.

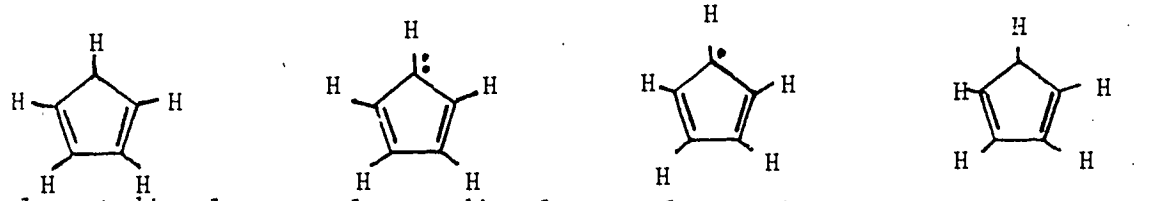
It is more correctly represented as:

SIP No. 15
Tape 1 - Work Sheet

Example No. 11



Example No. 12



cyclopentadienyl cation | cyclopentadienyl anion | cyclopentadiene free radical | cyclopentadiene

No of π electrons

_____ is probably aromatic and should be represented as _____

Assignment No. 1

Complete the following table:

	Hybridization on the C atom	bond angle (degree)	bond length *	Shape
ethane				
ethylene				
acetylene				
benzene				
cyclohexane				

*label as 1,2,3,4, where 1 means the LONGEST bond and 5 means the SHORTEST bond

SIP No. 15
Tape 1 - Work Sheet

Assignment No. 2

Cyclooctatetraene decolarizes cold aqueous KM_nO_4, reacts with bromine to yield $C_8H_8Br_8$ and has a heat of combustion same as expected.

a) Is cyclooctatebraene aromatic? _____

b) Is it flat or puckered?

When cyclooctatetraene is treated with potassium, it yields a stable salt $2K^+ C_8H_8^{--}$.

c) Of what significance is the formation of this salt?

d) What shape would you predict for the $C_8H_8^{--}$ anion?

Assignment No. 3

The properties of furan commonly represented by  show that it is aromatic. Account for its aromaticity on the basis of orbital theory.

Self Instructional Package No. 15
Tape 1 - Answer Sheet

BENZENE-AROMATICITY

Assignment No. 1

ethane	Sp^3	109.5	1	tetrahedrol
ethylene	Sp^2	120.	4	flat-planar
acetylene	Sp	180.	5	flat-linear
cyclohexane	Sp^3	109.5	~ 1	puckered
benzene	Sp^2	120.	3	flat

Assignment No. 2

a) No (it undergoes addition reactions readily, shows no indication of high stability and has 8 π e instead of 6 or 10)

b) puckered

c) it indicates the very high stability of the $C_8H_8^{--}$ anion, or in other words it implies its aromatic character

d) flat

Assignment No. 3

It is a ring compound with a homogeneous cyclic cloud of π electron density that contains 6 electrons - four π electrons from the two double bonds and two electrons from oxygen.

Self Instructional Package No. 15
Tape 2 - Work Sheet

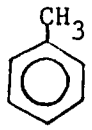
Then shall our names, Familiar in his mouth as household words..... Be in their flowing cups freshly remember'd.

---Shakespeare

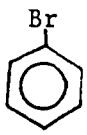
BENZENE - AROMATICITY

NOMENCLATURE

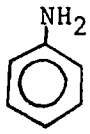
Example No. 1



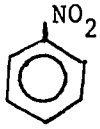
Methyl Benzene



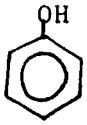
Bromobenzene



Aminobenzene



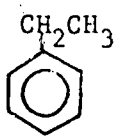
Nitrobenzene

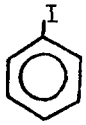


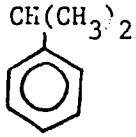
Hydroxy Benzene

Assignment No. 1

Assign the IUPAC names to the compounds listed below:

a) 

b) 

C) 

d) 

Assignment No. 2

Draw the structural formulas which correspond to the IUPAC names listed below:

a) isobutyl benzene

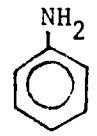
b) t-butyl benzene

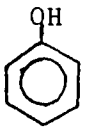
c) nitrobenzene

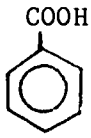
d) bromobenzene

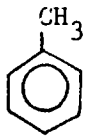
Assignment No. 2 (continued)

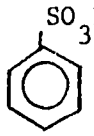
Example No. 2


Aniline

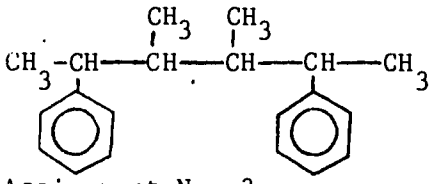
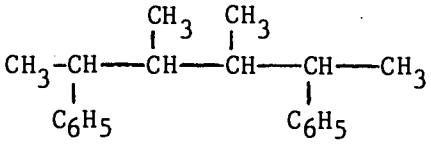

Phenol


Benzoic Acid


Toluene

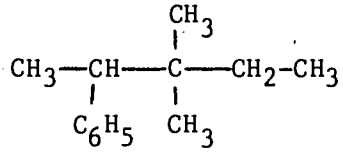

Benzene Sulfonic Acid

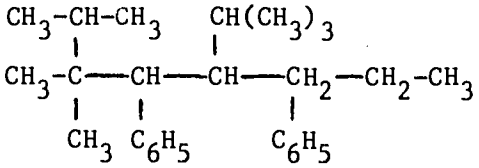
Example No. 3


OR


Assignment No. 3

Assign thecorrect IUPAC names to the compounds below:

a) 

b) 

Assignment No. 4

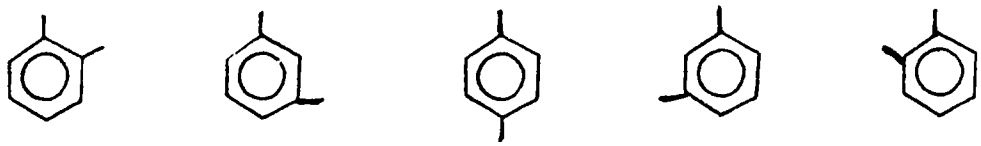
a) 2,4-diphenyl-3-isobutyl heptane

b) 3,5-diphenyl-4-methyl-2-hexene

c) 2,4-diphenyl-2,4-hexadiene

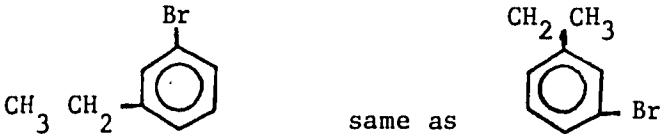
SIP No. 15
Tape 2 - Work Sheet

Example No. 4



1.2	1.3	1.4	1.5	1.6
Ortho	Meta	Para	Meta	Ortho
O-	m-	p-	m-	O-

Example No. 5

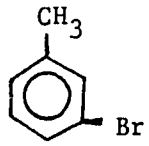


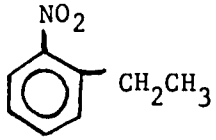
m-bromo ethyl benzene

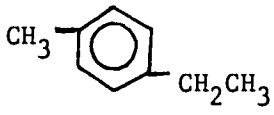
m-ethyl bromo benzene

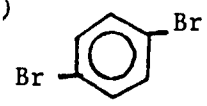
Assignment No. 5

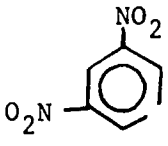
Assign IUPAC names using both number notations and the O, M, P notation to the compounds below:

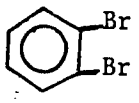
a) 

c) 

e) 

b) 

d) 

f) 

SIP No. 15
Tape 2 - Work Sheet

Assignment No. 6

Draw the structural formulas which correspond to the compounds below:

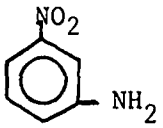
a) O-dinitro benzene

b) p-nitro bromo benzene

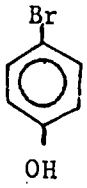
c) m-difluoro benzene

d) 1-methyl-3-iodo benzene

Example No. 6



m-nitroaniline



p-bromophenol

Assignment No. 7

Draw the structural formulas which correspond to the names listed below:

a) m-iodo benzoic acid

b) p-nitro toluene

Assignment No. 7 (continued)

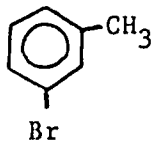
c) p-nitro benzenesulfonic acid

d) O-fluoro aniline

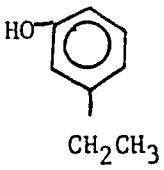
Assignment No. 8

Assign the correct IUPAC names to the structural formulas below:

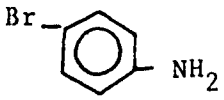
a)



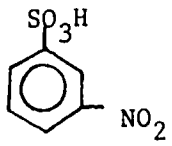
b)



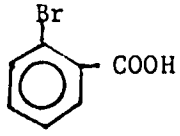
c)



d)



e)

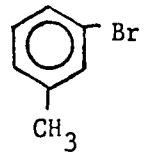


SIP No. 15
Tape 2 - Work Sheet

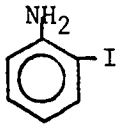
Inert Irma

Assignment No. 9

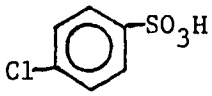
Inert Irma was asked to assign correct IUPAC names to a number of compounds. She has made several mistakes. It is your task now to identify and correct her mistakes.

a) 

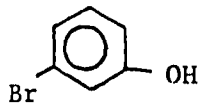
1-bromo-3-methyl benzene

b) 

2-iodo amino benzene

c) 

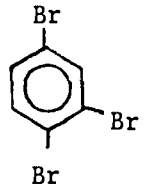
p-chloro benzene sulfonic acid

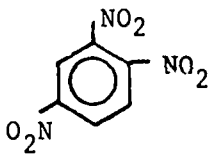
d) 

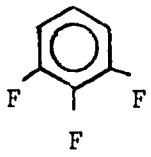
p-bromo phenol

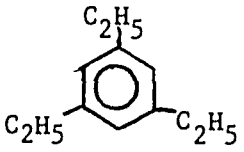
Assignment No. 10

Assign the correct IUPAC names to the structural formulas listed below:

a) 

b) 

c) 

d) 

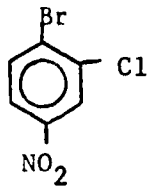
SIP No. 15
Tape 2 - Work Sheet

Assignment No. 11

Draw the structural formulas and name all the possible isomers of:

a) tribromo benzene and b) tetrabromo benzene

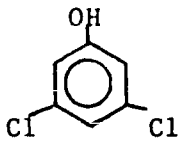
Example No. 7



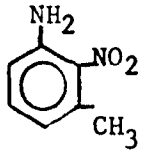
2-chloro-4-nitro bromo benzene or

3-chloro-4-bromonitro benzene

Example No. 8



3,5-dichloro phenol



2-nitro-3-methyl aniline

Assignment No. 12

Draw the structural formulas which correspond to the IUPAC names listed below:

a) 2,4-dinitro phenol

b) 2-ethyl-4-bromo aniline

c) 3-bromo-5-nitro benzene sulfonic acid

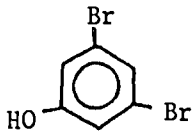
Assignment No. 12 (continued)

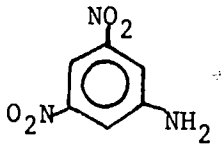
d) 2,4,6-trinitro benzoic acid

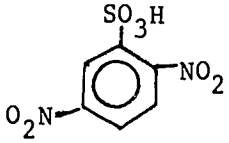
e) 2,3-dinitro-5-bromo toluene

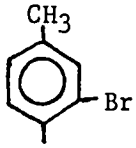
Assignment No. 13

Assign the correct IUPAC names to the structural formulas below:

a) 

b) 

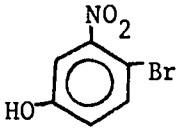
c) 

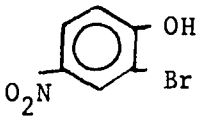
d) 

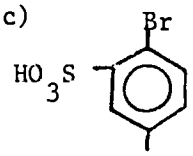
I

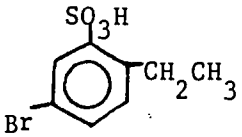
Assignment No. 14

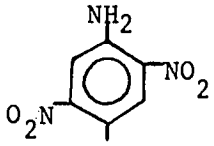
Match the structural formula on the left with the correct IUPAC name on the right.

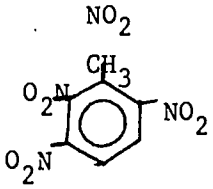
a) 

b) 

c) 

d) 

e) 

f) 

A. 2,4,5-trinitro aniline

B. 2,3,6-trinitro toluene

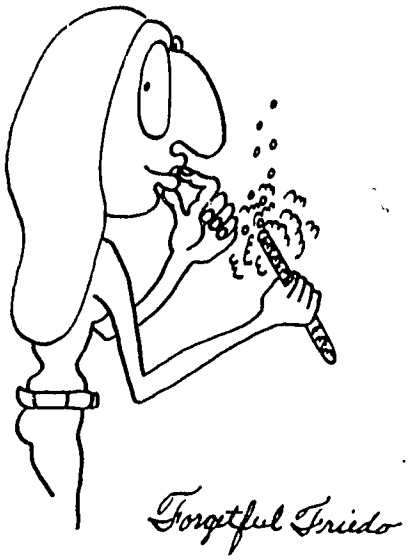
C. 2-bromo-4-nitro phenol

D. 2-ethyl-5-bromo benzene sulfonic acid

E. 3-nitro-4-bromo phenol

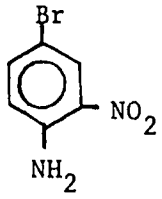
F. 2-bromo-5-ethyl benzene sulfonic acid

SIP No. 15
Tape 2 - Work Sheet

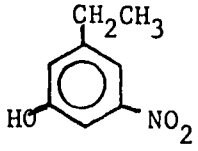


Assignment No. 15

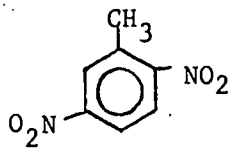
Forgetful Frieda has been asked to assign correct IUPAC names to the compounds below. Her answers are not quite correct. Complete and correct her answers.

a) 

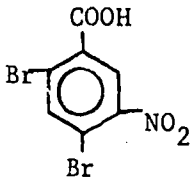
O-nitro-p-bromo aniline

b) 

3-nitro-5-hydroxy ethyl benzene

c) 

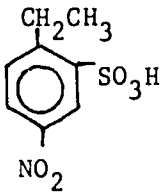
2,5-nitro toluene

d) 

m-nitro-2,4-bromo benzoic acid

Assignment No. 15 (continued)

e)



2-ethyl-4-nitro benzene
sulfonic acid

Assignment No. 16

Draw the structures and name all the theoretically possible structural isomers of:

a) Benzene with the following three substituents: Br, NO_2, CH_3

b) Benzene with the following four substituents: Cl, Cl, OH

c) Benzene with the following three substituents: NH_2, Br, NO_2

Self Instructional Package No. 15
Tape 2 - Answer Sheet

BENZENE-AROMATICITY

Nomenclature

Assignment No. 1

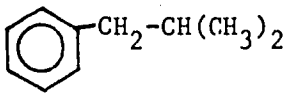
a) ethylbenzene

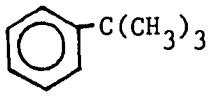
b) iodobenzene

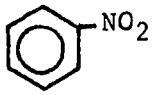
c) isopropylbenzene

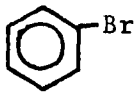
d) fluorobenzene

Assignment No. 2

a) 

b) 

c) 

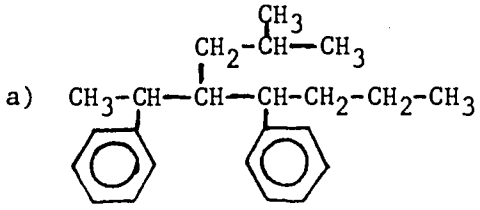
d) 

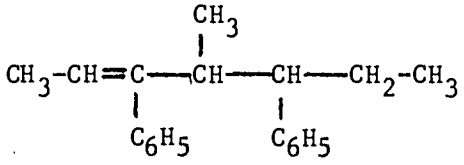
Assignment No. 3

a) 2-phenyl-3,3-dimethyl pentane

b) 2,3,3-trimethyl-5-t-butyl-4,6-diphenyl octane

Assignment No. 4

a) 

b) 

SIP No. 15
Tape 2 - Answer Sheet

Assignment No. 4 (continued)

c) $CH_3-C(C_6H_5)=CH-C(C_6H_5)=CH-CH_3$

Assignment No. 5

a) 1-bromo-3-methyl benzene; m-bromo, methyl benzene

b) 1,4-dibromobenzene; p-dibromobenzene

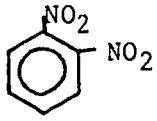
c) 1-nitro-2-ethyl benzene; O-nitroethylbenzene

d) 1,3-dinitrobenzene; m-dinitrobenzene

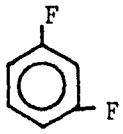
e) 1-methyl-4-ethyl benzene; p-methyl ethylbenzene

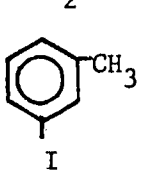
f) 1,2-dibromobenzene; O-dibromobenzene

Assignment No. 6

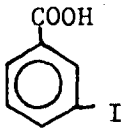
a) 

b) 

c) 

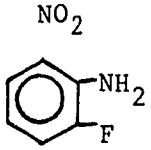
d) 

Assignment No. 7

a) 

b) 

c) 

d) 

SIP No. 15
Tape 2 - Answer Sheet

Assignment No. 8

a) m-bromotoluene

b) m-ethylphenol

c) p-bromo aniline

d) m-nitrobenzenesulfonic acid

e) O-bromo benzoic acid

Assignment No. 9

a) m-bromo toluene (1-bromo-3-methyl benzene is also correct)

b) o-iodoaniline

c) correct

d) m-bromophenol

Assignment No. 10

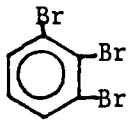
a) 1,2,4-tribromobenzene

b) 1,2,5-trinitrobenzene

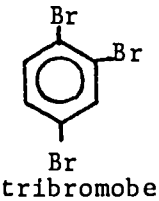
c) 1,2,3-trifluorobenzene

d) 1,3,5-triethylbenzene

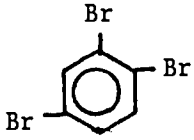
Assignment No. 11

a) 

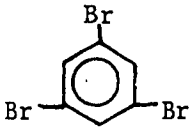
1,2,3-tribromobenzene



1,2,4-tribromobenzene



1,2,5-tribromo-benzene

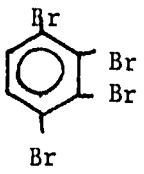


1,3,5-tribromobenzene

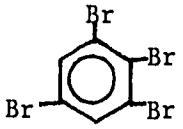
SIP No. 15
Tape 2 - Answer Sheet

Assignment No. 11 (continued)

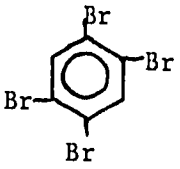
b)



1,2,3,4-tetrabromo benzene



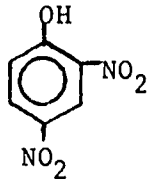
1,2,3,5-tetrabromo-benzene



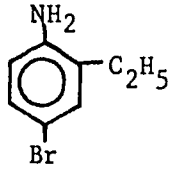
1,2,4,5-tetrabromo benzene

Assignment No. 12

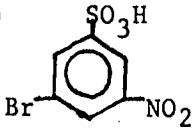
a)



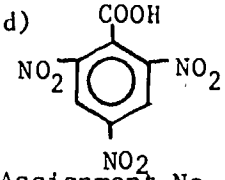
b)



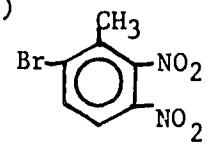
c)



d)



e)



Assignment No. 13

a) 3,5-dibromophenol

b) 2,5-dinotrobenzenesulfonic acid

c) 3,5-dinitro aniline

d) 3-bromo-4-iodo-toluene

Assignment No. 14

a)	E	d)	D or F
b)	C	e)	A
c)	D or F	f)	B

SIP No. 15
Tape 2 - Answer Sheet

Assignment No. 15

a) 2-nitro-4-bromo aniline

b) 3-ethyl-5-nitro phenol

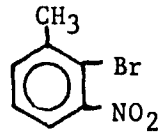
c) 2,5-dinitro toluene

d) 2,4-dibromo-5-nitro benzoic acid

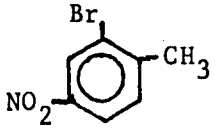
e) 2-ethyl-5-nitro benzenesulfonic acid

Assignment No. 16

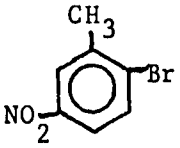
a)



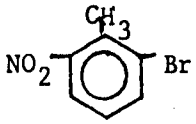
2-bromo-3-nitro toluene



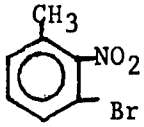
2-bromo-4-nitro toluene



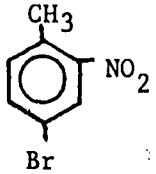
2-bromo-5-nitro toluene



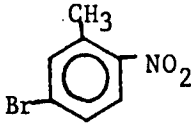
2-bromo-6-nitro toluene



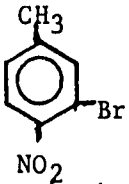
2-nitro-3-bromo toluene



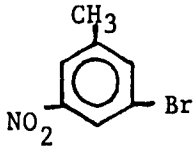
2-nitro-4-bromo toluene



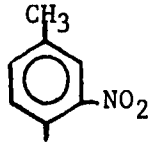
2-nitro-5-bromo toluene



3-bromo-4-nitro toluene

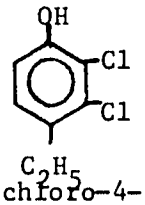


3-bromo-5-nitro toluene

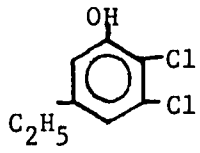


3-nitro-4-bromo toluene

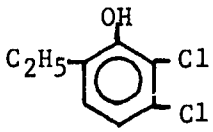
b)



2,3-dichloro-4-ethyl phenol



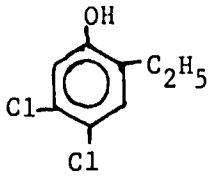
2,3-dichloro-5-ethyl phenol



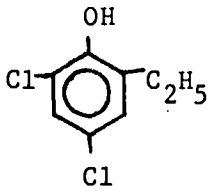
2,3-dichloro-6-ethyl phenol

Assignment No. 16 (continued)

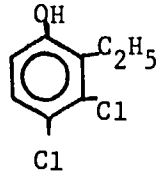
b)



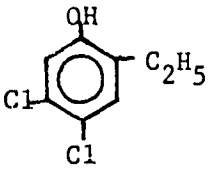
2,4-dichloro-5-ethyl phenol



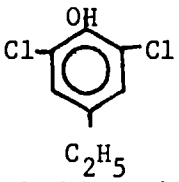
2,4-dichloro-6-ethyl phenol



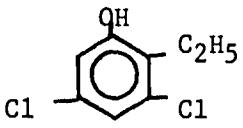
2-ethyl-3,4-dichloro phenol



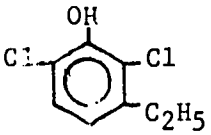
2-ethyl-4,5-dichloro phenol



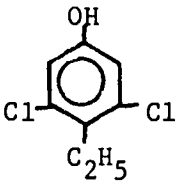
2,6-dichloro-4-ethyl phenol



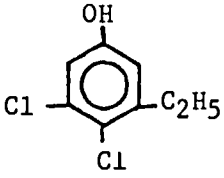
3,5-dichloro-2-ethyl phenol



2,6-dichloro-3-ethyl phenol

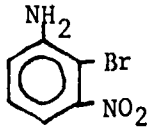


3,5-dichloro-4-ethyl phenol

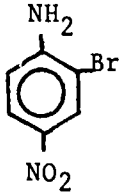


3,4-dichloro-5-ethyl phenol

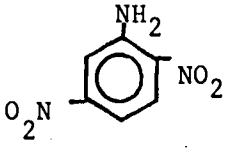
c)



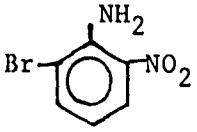
2-bromo-3-nitro aniline



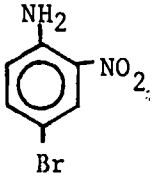
2-bromo-4-nitro aniline



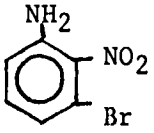
2-bromo-5-nitro aniline



2-bromo-6-nitro aniline



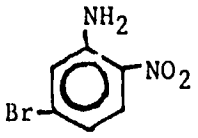
2-nitro-4-bromo aniline



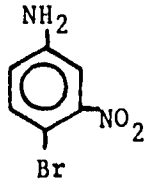
2-nitro-3-bromo aniline

Assignment No. 16 (continued)

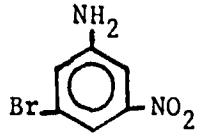
c)



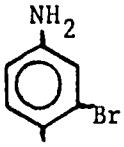
2-nitro-5-bromo aniline



3-nitro-4-bromo aniline



3-nitro-5-bromo aniline



3-bromo-4-nitro aniline

Explanations, explanatory of things explained.
---A. Lincoln

BENZENE AROMATICITY

Electrophilic Aromatic Substitution

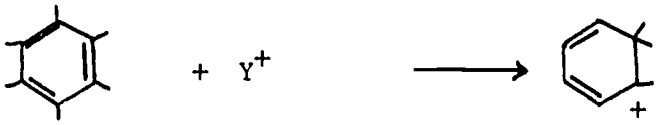
Example No. 1 - Mechanism of the electrophilic aromatic substitution

Step 1a - Formation of the electrophile

$$YZ \longrightarrow Y^{+} + Z^{-}$$

electrophile nucleophile

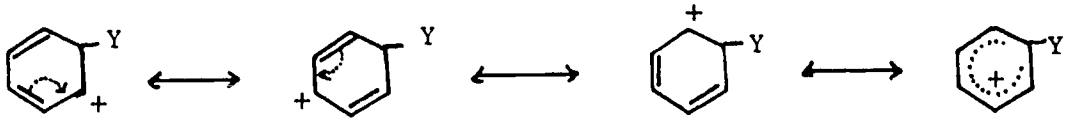
Step 1 - Attack of the electrophile on the benzene ring and formation of the carbonium ion intermediate



electrophile I

(electron seeking reagent) carbonium ion intermediate

Resonance stabilization of the carbonium ion I --



I II III IV

\+ is in o-position relative to Y + is in p-position relative to Y + is in o-position relative to Y

Step 2 - Abstraction of H^{+} and regeneration of the aromatic character

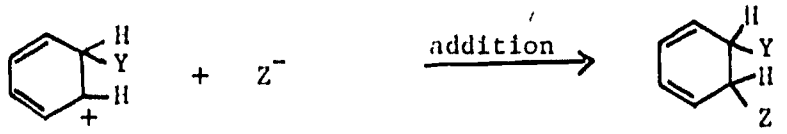
a) Substitution

I monosubstituted benzene

Step 2 - (continued)

Two possibilities:

b) addition -



I

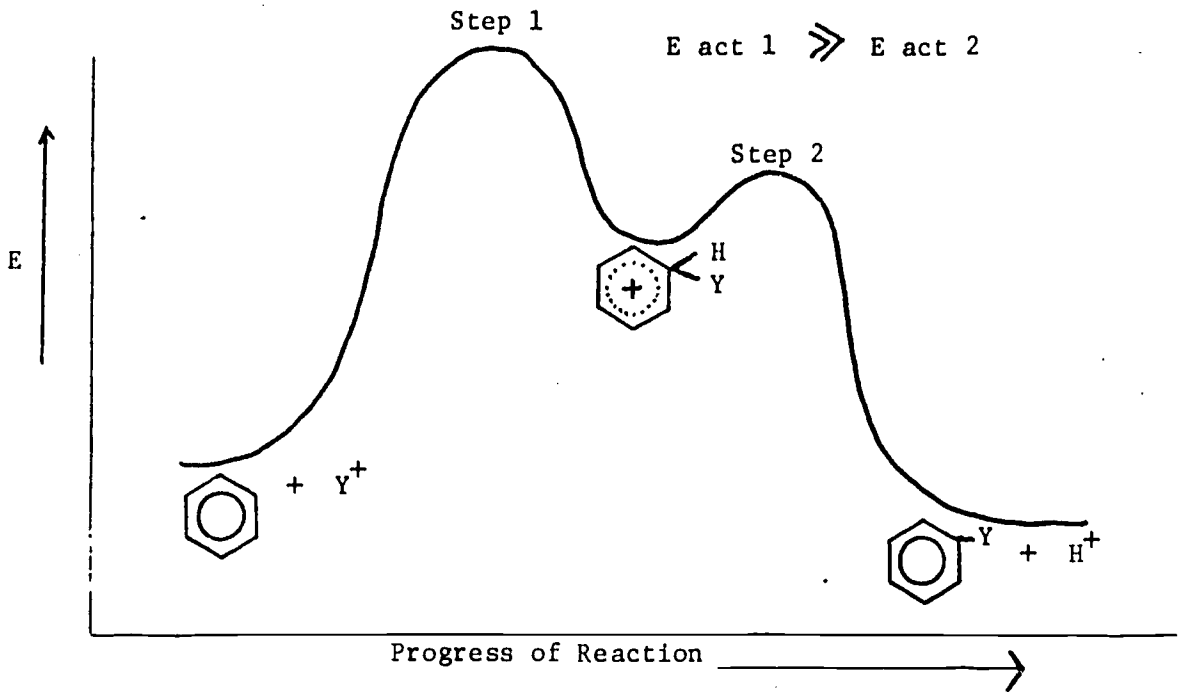
Example No. 2 - Isotope effect

The rate determining step in the electrophilic aromatic substitution is the attack of the electrophile on the benzene ring and the formation of the intermediate carbonium ion.

if C—H bond cleavage is NOT the rate determining step there will be NO deuterium isotope effect observed.

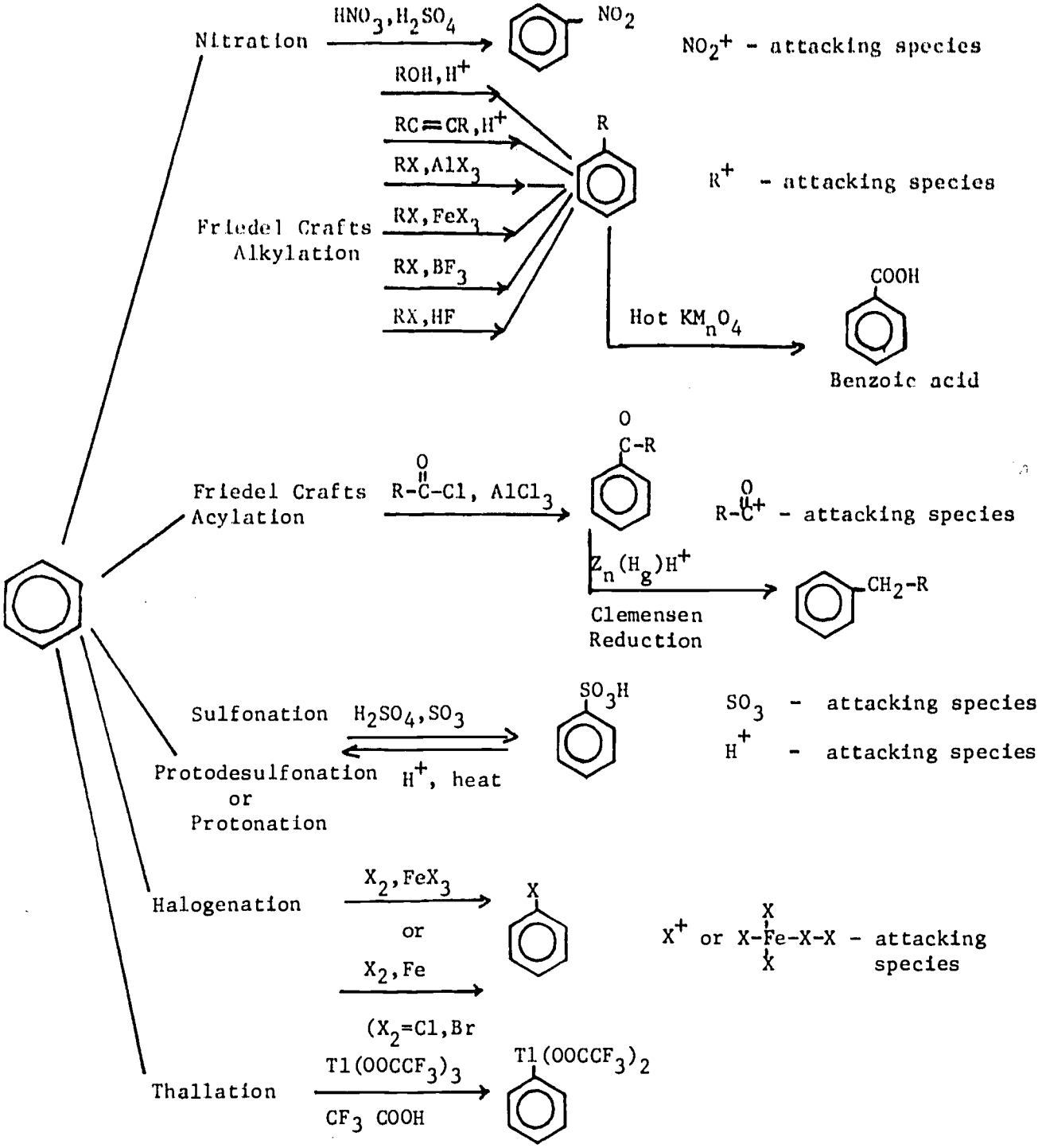
if C—H bond cleavage IS the rate determining step there will be a deuterium isotope effect observed.

Example No. 3 - Energy diagram for the electrophilic aromatic substitution nitration, Friedel-Crafts alkylation and acylation, thallation)



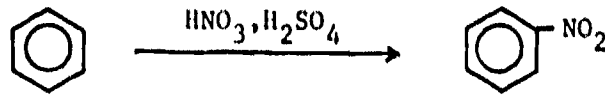
Step 1 or the formation of carbonium ion is the rate-determining step. All carbonium ions go to product. There is no isotope effect. The reaction is irreversible.

Example No. 4 - Electrophilic Aromatic Substitution Reactions of Benzene



Example No. 5 - Nitration Mechanism

Overall Reaction:



Step 1 - Generation of the attacking species - NO_2^+

a) $HO{-}NO_2 + H{-}OSO_3H \longrightarrow H_2O^+{-}NO_2 + \bar{O}SO_3H$

b) $H_2O^+{-}NO_2 \longrightarrow H_2O + NO_2^+$

c) $H_2O: + H{-}OSO_3H \longrightarrow H_3O^+ + \bar{O}SO_3H$

---

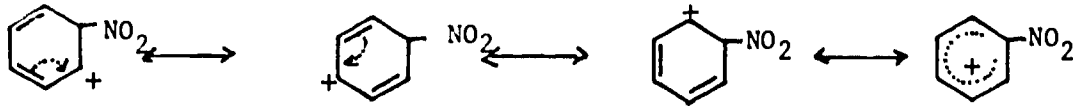
a) + b) + c):

$$HNO_3 + H_2SO_4 + H_2O^+NO_2 + H_2O + H_2SO_4 \longrightarrow H_2O^+NO_2 + HSO_4^- + H_2O + H_3O^+ + HSO_4$$

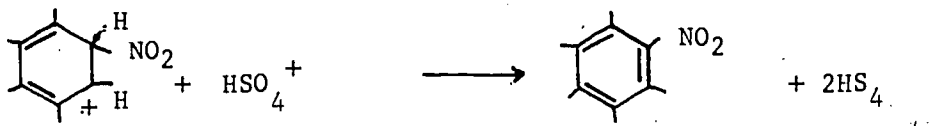
$$HNO_3 + 2H_2SO_4 \longrightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$$

Step 2 - Formation of the carbonium Ion

Step 2a - Resonance stabilization of the carbonium ion

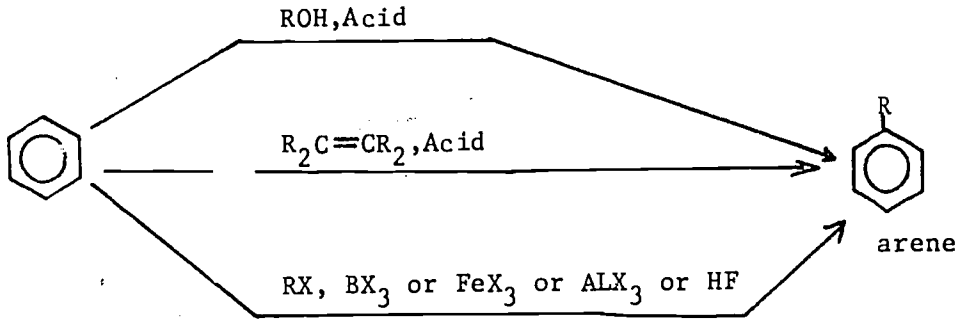


Step 3 - Abstraction of hydrogen and regeneration of the aromatic character



Example No. 6 - Friedel-Crafts Alkylation Reaction

Overall Reaction:



Step 1 - Formation of the attacking species

1. $R-\overset{|}{C}-OH + H^+ \longrightarrow R-\overset{|}{C}-\overset{+}{O}H_2 \longrightarrow R-\overset{|}{C}^+ + H_2O$

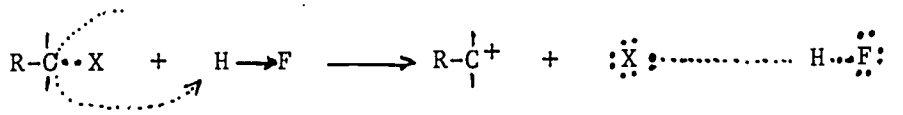
2. $>C=C< + H^+ \longrightarrow -\overset{|}{C}-\overset{|}{C}^+ \quad (H)$

3. $R-\overset{|}{C}\cdots X + \overset{X}{\underset{X}{B}}-X \longrightarrow R-\overset{|}{C}^+ + X:\overset{X}{\underset{X}{B}}:X$

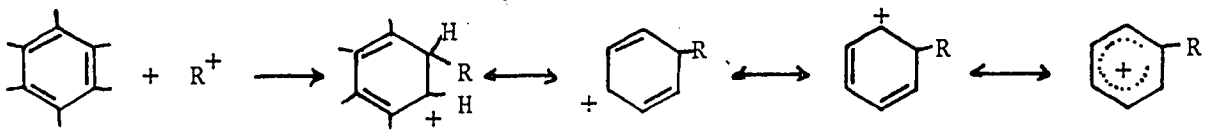
$R-\overset{|}{C}\cdots X + \overset{X}{\underset{X}{Fe}}\cdots X \longrightarrow R-\overset{|}{C}^+ + X:\overset{X}{\underset{X}{Fe}}:X$

$R-\overset{|}{C}\cdots X + \overset{X}{\underset{X}{Al}}:X \longrightarrow R-\overset{|}{C}^+ + X:\overset{X}{\underset{X}{Al}}:X^-$

Step 1 - Formation of the attacking species (continued)



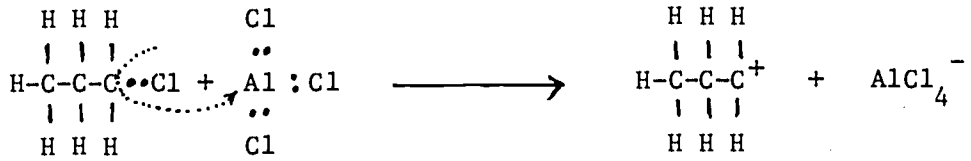
Step 2 - Formation of the carbonium ion and its resonance stabilization



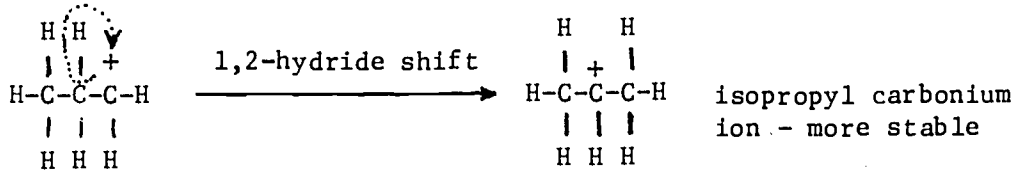
Step 3 - Regeneration of the aromatic character

Example No. 7 - Friedel-Crafts Alkylation Reaction

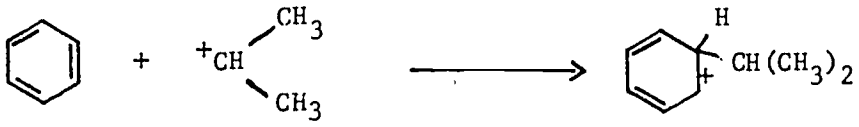
Step 1



n-propyl carbonium ion

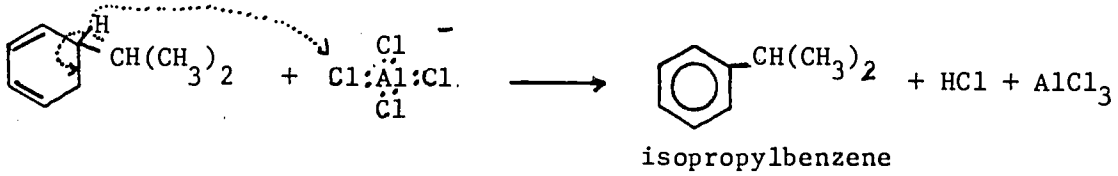


Step 2 - Attack of the isopropyl carbonium ion on the benzene ring



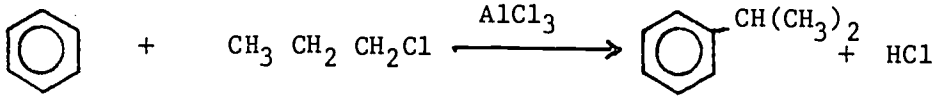
SIP No. 15
Tape 3 - Work Sheet

Step 3 - Abstraction of H^+

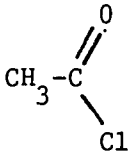


isopropylbenzene

Overall Reaction:



Assignment No. 1

Write the mechanism for the Friedel-Crafts reaction of benzene with acetyl-chloride  in the presence of aluminim trichloride.

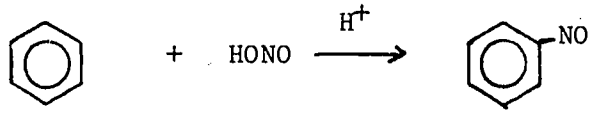
Assignment No. 2

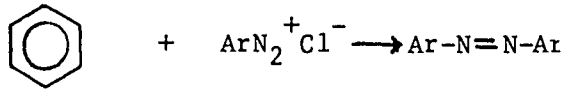
Write the mechanism for the reaction of benzene with 1-chloro-2-methyl propane in presence of $AlCl_3$.

SIP No. 15
Tape 3 - Work Sheet

Assignment No. 3

Suggest a likely electrophile in each case and write the reactions to show how they are formed. Write the step-by-step mechanism for one of the reactions below.

a) 

b) 

Example No. 8 - Sulfonation Reaction

Step 1 - Formation of the electrophile

(1) $H\ddot{O}SO_3H + HOSO_3H \longrightarrow H_2\overset{+}{O}SO_3H + HSO_4^-$

(2) $H_2\overset{+}{O}SO_3H \longrightarrow H_2O + HSO_3^+$

(3) $HSO_3^+ + H_2O \longrightarrow H_3O^+ + SO_3$

---

(1) + (2) + (3):
$HOSO_3H + HOSO_3H + H_2\overset{+}{O}SO_3H + HSO_3^+ + H_2O \longrightarrow$

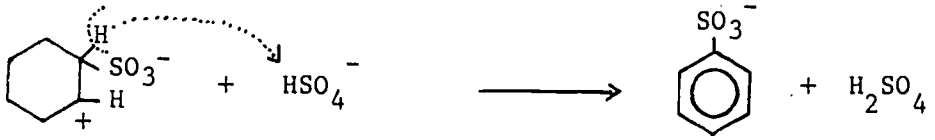
$H_2\overset{+}{O}SO_3H + HSO_4^- + H_2O + HSO_3^+ + H_3O^+ + SO_3$

Combined: $HOSO_3H + HOSO_3H \longrightarrow H_3O^+ + SO_3 + HSO_4^-$

SIP No. 15
Tape 3 - Work Sheet

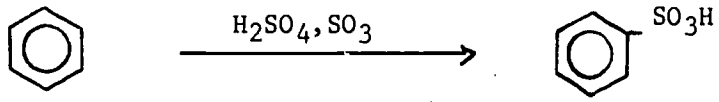
Step 2 - Formation of the carbonium ion

Step 3 - Dissociation of hydrogen positive ion and regeneration of the aromatic character



Step 4

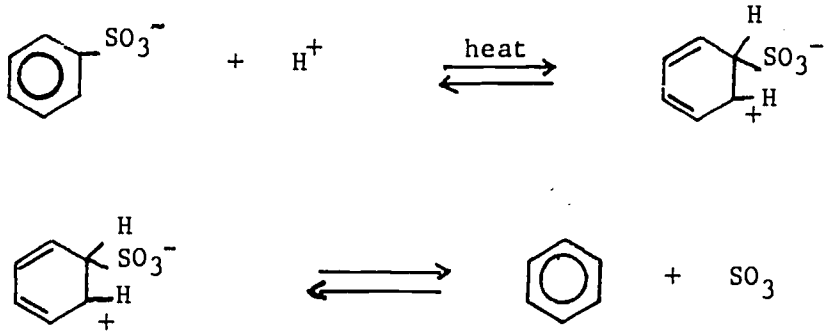
Overall Reaction:



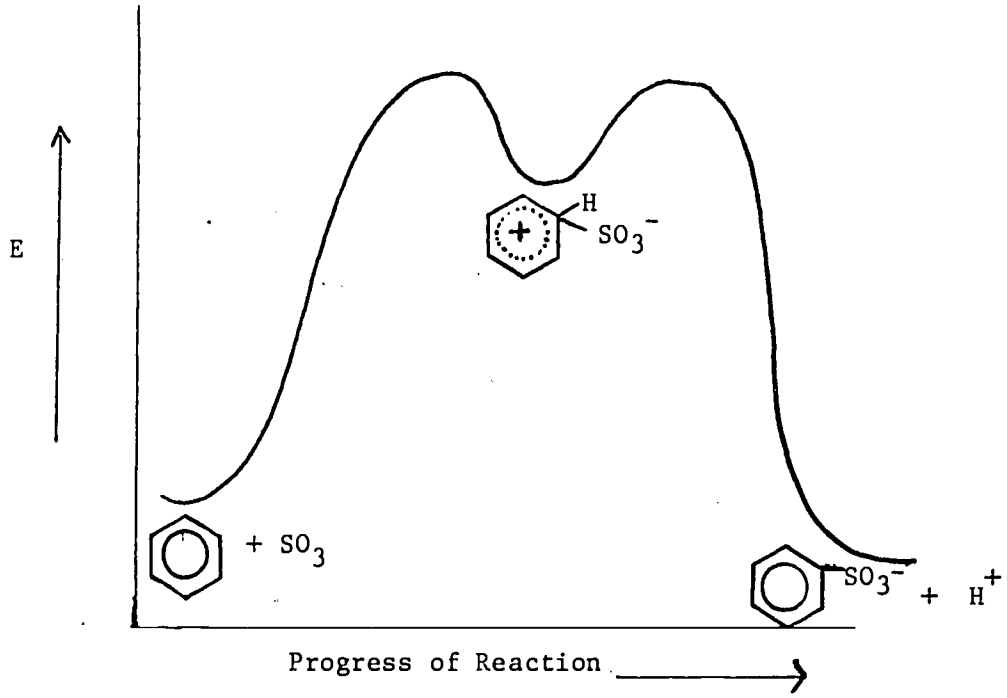
Assignment No. 4

Nitration of benzene can be performed with nitric acid alone rather than the acid mixture. Write an equation for the generation of NO_2^+ from nitric acid alone.

Example No. 9 - Desulfonation reaction



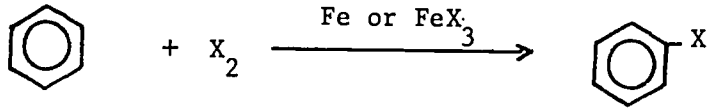
Example No. 10 - Energy diagram for the sulfonation reaction.



Carbonium ion can go on to product or to revert to the starting material. The reaction is reversible because the two Eact's have approximately the same values. Small isotope effect is observed due to the reverse or desulfonation reaction.

Example No. 11 - Halogenation Reaction

Overall reaction:

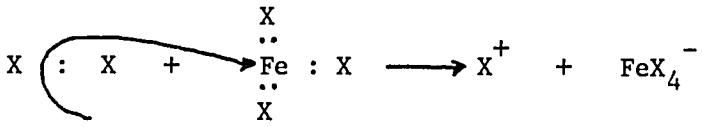


X can be Br or Cl

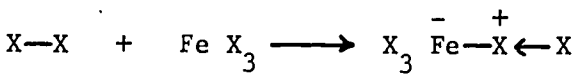
Step 1 - Formation of the electrophile

$$(2Fe + 3X_2 \longrightarrow 2\ Fe\ X_3)$$

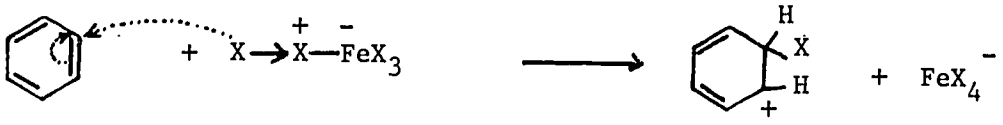
a possibility -



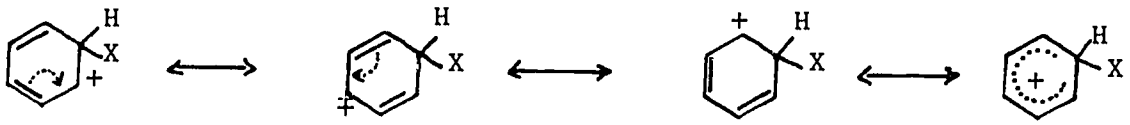
more likely the electrophile is -



Step 2 - Formation of the carbonium ion

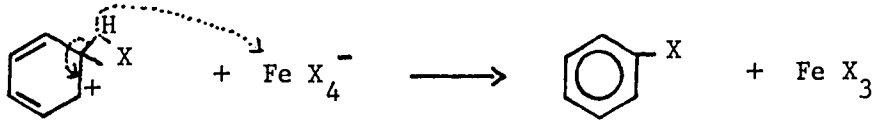


Stabilization of the carbonium ion



SIP No. 15
Tape 3 - Work Sheet

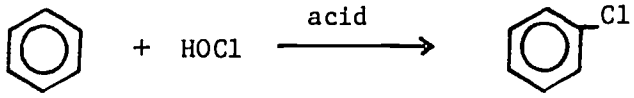
Step 3 - Abstraction of hydrogen positive ion



regenerated catalyst

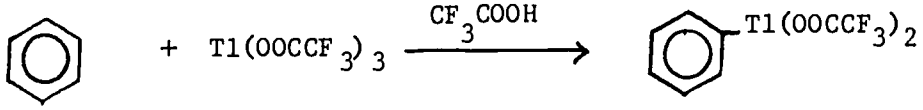
Assignment No. 5

Write the mechanism for the reaction below. Explain the function of the acid here.



hypochlorous acid

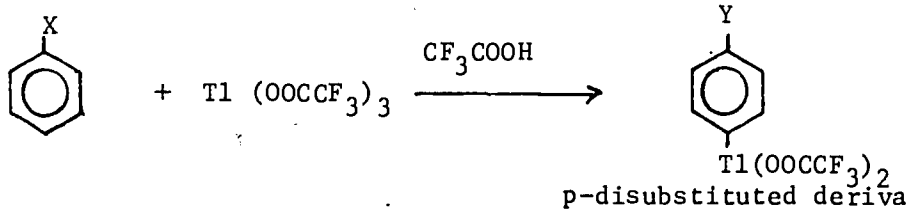
Example No. 12 - Thallation



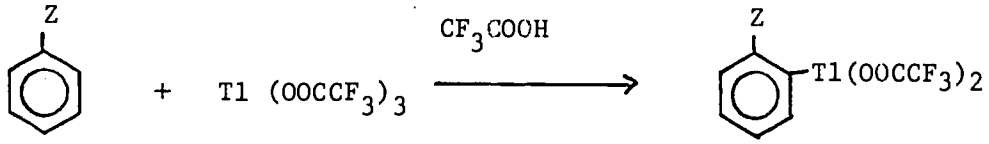
phenylchallium difluoroacetate

Example No. 12 - Thallation (continued)

Thallation reaction is highly regiospecific -



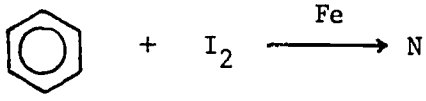
p-disubstituted derivative exclusively

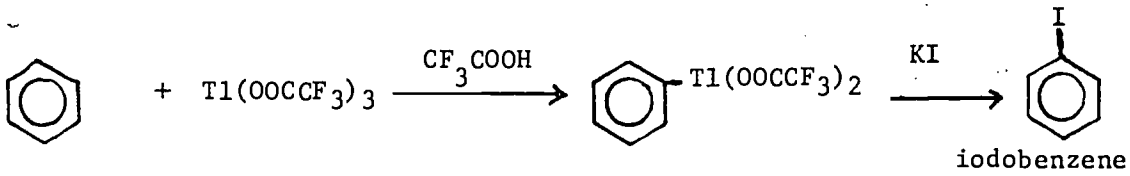


o-disubstituted derivative exclusively

(Z = )

Thallation can be used in a multi-step synthesis of iodobenzene.

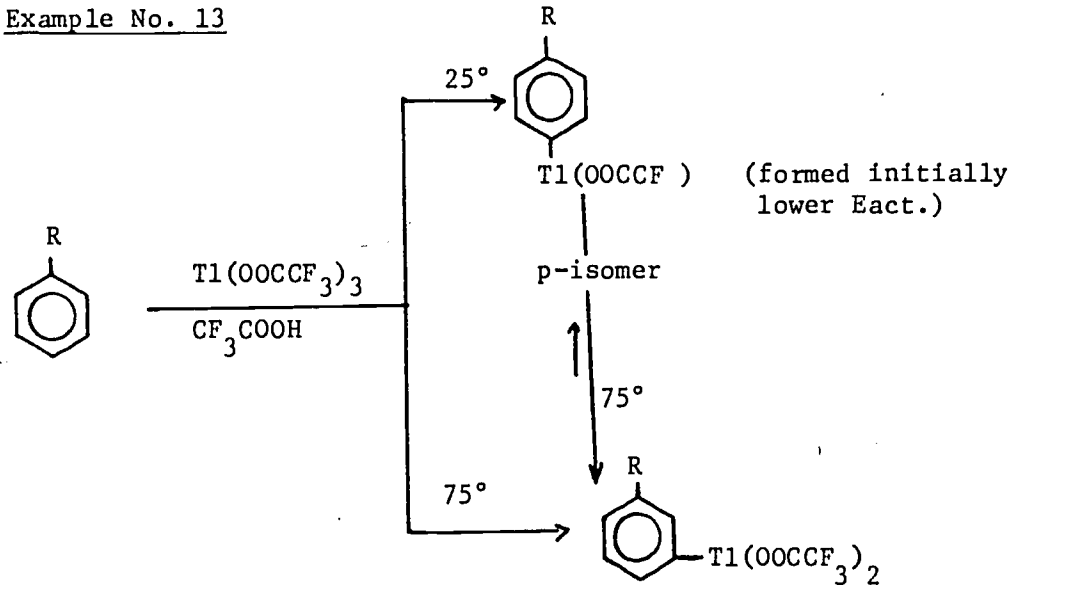




iodobenzene

SIP No. 15
Tape 3 - Work Sheet

Example No. 13



m-isomer (more stable)

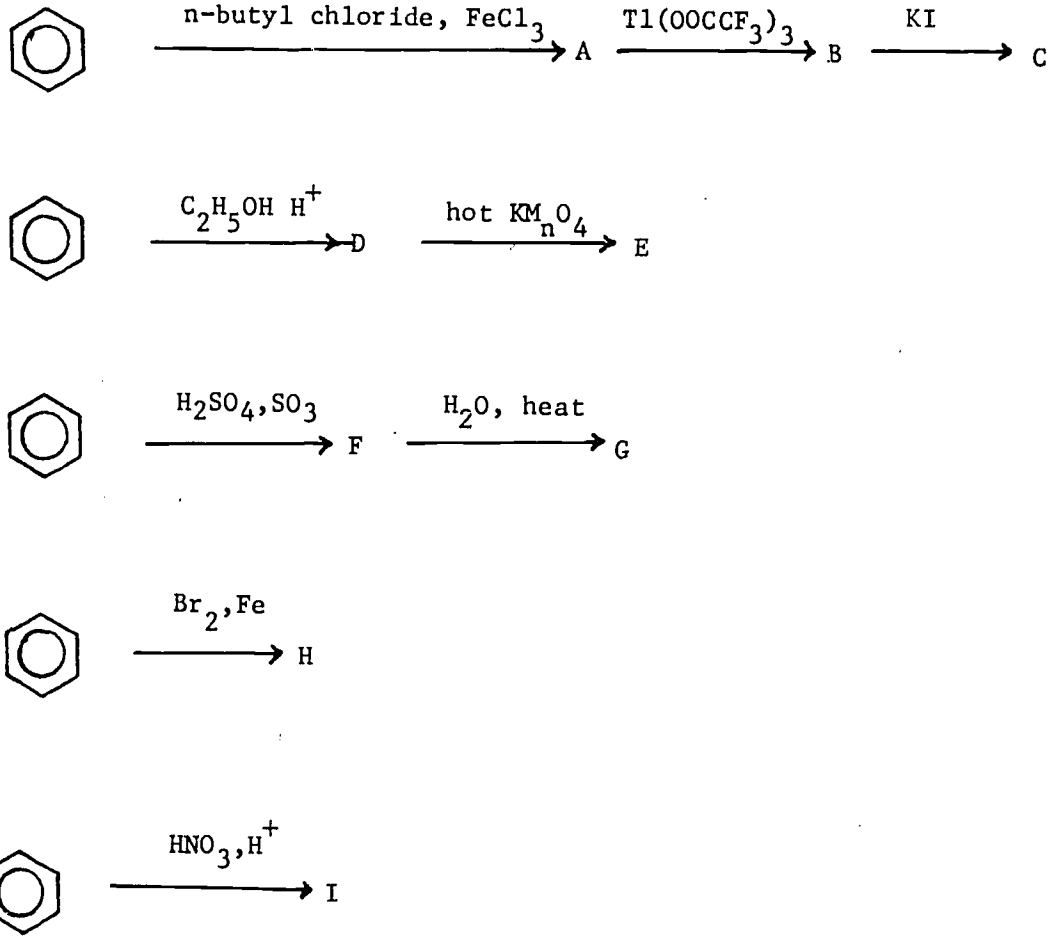
Assignment No. 6

Outline all the steps in the synthesis of p-iodotoluene from benzene.

SIP No. 15
Tape 3 - Work Sheet

Assignment No. 7

Identify compounds A through I in the following reactions:



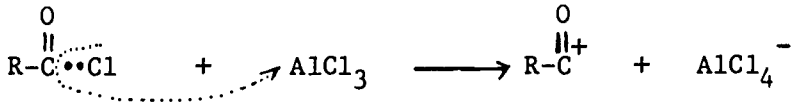
Self Instructional Package No. 15
Tape 3 - Answer Sheet

BENZENE - AROMATICITY

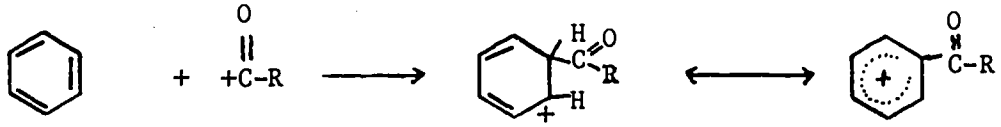
Electrophilic Aromatic Substitution

Assignment No. 1 - Friedel-Crafts acylation reaction

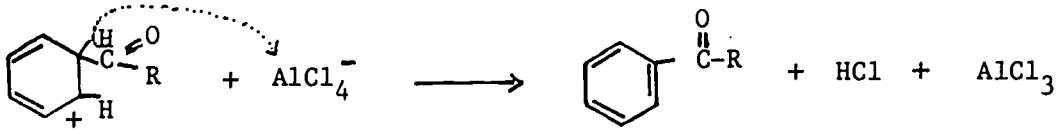
Step 1 - formation of the electrophile



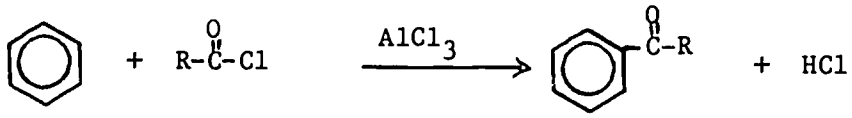
Step 2 - formation of the carbonium ion



Step 3 - loss of H^+ and regeneration of the aromatic character

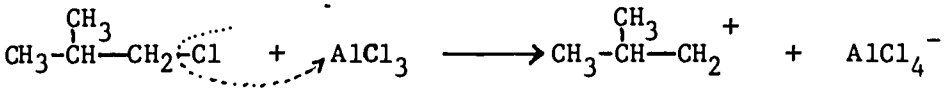


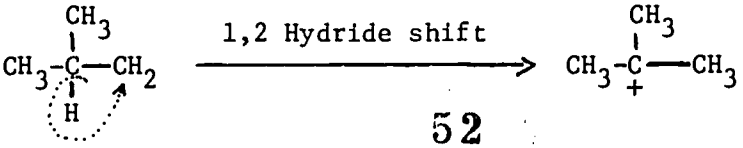
Overall reaction:



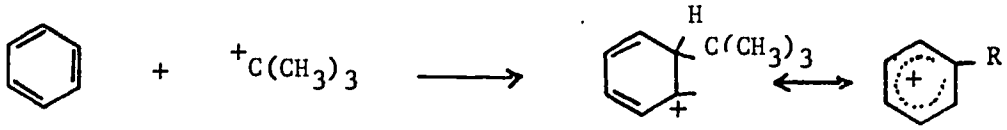
Assignment No. 2 -

Step 1

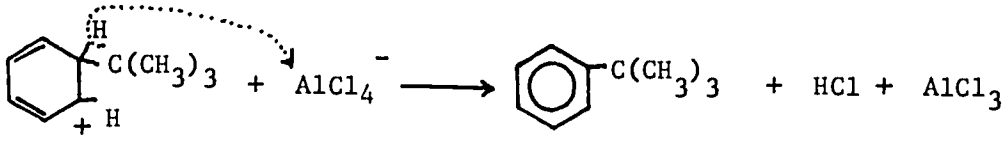




Step 2

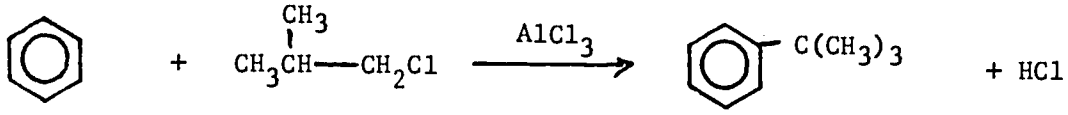


Step 3 - Dissociation of H^+ and regeneration of aromatic character



regenerated catalyst

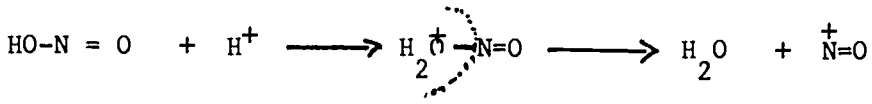
Overall reaction:



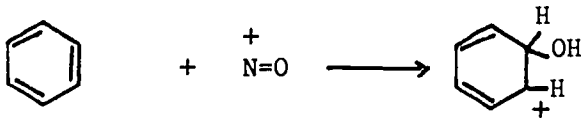
Assignment No. 3

a) electrophile is NO

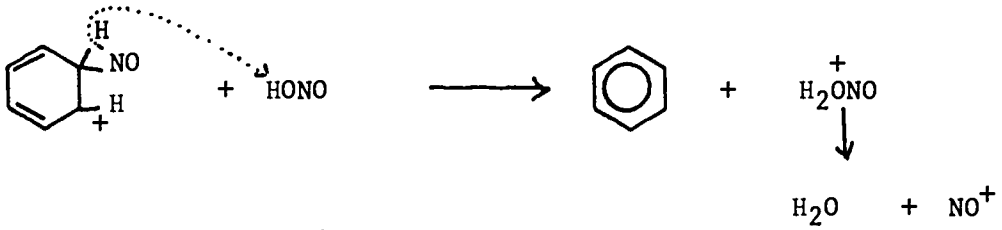
Step 1



Step 2

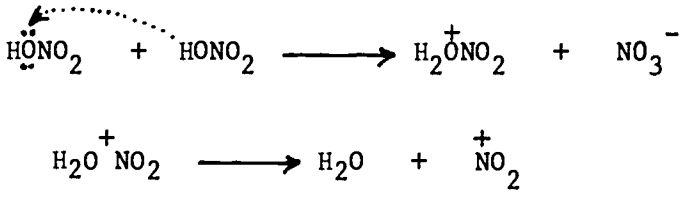


Step 3



b) electrophile is ArN_2^+

Assignment No. 4



$HONO_2 + HONO_2 + H_2O^+NO_2 \longrightarrow H_2O^+NO_2 + NO_3^- + H_2O + NO_2^+$

Combined: $2\ HNO_3 \longrightarrow H_2O + NO_2^+ + NO_3^-$

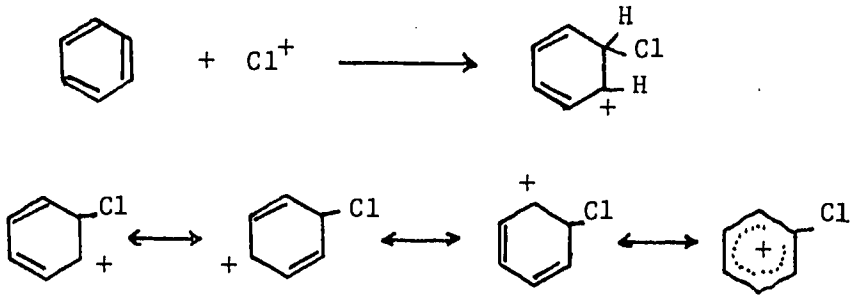
Assignment No. 5

Step 1 -

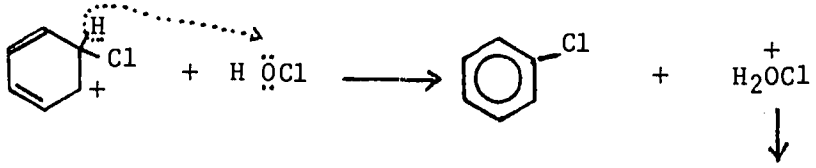
$H_2OCl \longrightarrow H_2O + Cl^+$

SIP No. 15
Tape 3 - Answer Sheet

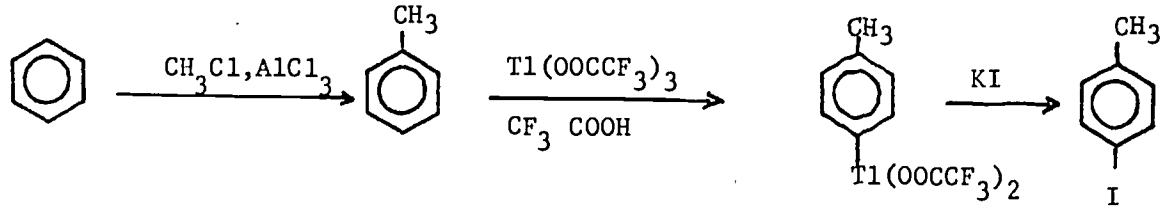
Step 2



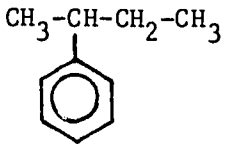
Step 3



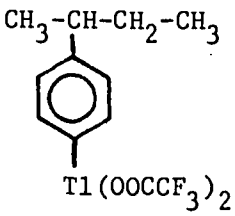
Assignment No. 6



Assignment No. 7

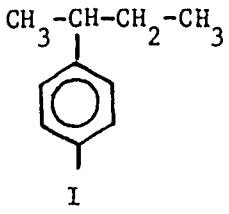
A 

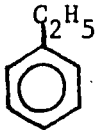
2-phenyl butane or sec. butyl benzene

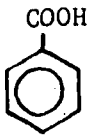
B 

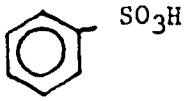
p-sec. butyl phenyl thalliumdifluoro acetate

Assignment No. 7 (continued)

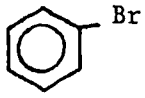
C  p-iodo-sec. butyl benzene

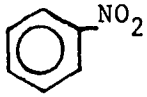
D  ethylbenzene

E  benzoic acid

F  benzenesulfonic acid

G  benzene

H  bromobenzene

I  nitrobenzene

Self Instructional Package No. 15
Form D - Progress Check Evaluation

BENZENE-AROMATICITY

Identify the statements below as True or False by placing a capital T or a capital F in the space to the left.

1. _____ Friedel-Crafts alkylation reaction is a reaction of benzene with alkyl halide in presence of BF_3.

2. _____ Friedel-Crafts acylation reaction is a reaction of benzene with acetylchloride in presence of $AlCl_3$.

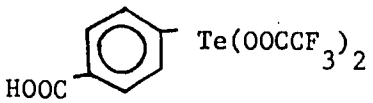
3. _____ In protodesulfonation reaction benzenesulfonic acid is converted into benzene.

4. _____ Resonance stabilization energy is the energy liberated due to the formation of resonance structures.

5. _____ The positive charge in the intermediate carbonium ion formed in the electrophilic aromatic substitution is delocalized over the entire ring.

6. _____ The great stability of benzene is caused by the overlap of p atomic orbitals and delocalization of π electrons over the entire ring.

7. _____ Thallation of benzoic acid would result almost exclusively in:



8. _____ Attacking species in an electrophilic aromatic substitution is an electron seeking reagent.

Blacken out the correct answer or answers in the questions below:

9. Select the facts that verify the structure of benzene.

   a) all carbon-carbon bonds have the same length.
   b) there is only one monosubstituted derivative of benzene.
   c) benzene shows lower than expected heat of combustion.
   d) there are three possible disubstituted derivatives of benzene.

10. Characteristic features for an aromatic compound are:

   a) it undergoes primarily addition reactions.
   b) it shows higher than expected heat of hydrogenation.
   c) all attached hydrogens are identical.
   d) it shows lower than expected heat of combustion.

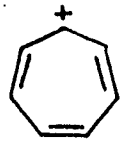
11. Select the species that would be expected to exhibit aromatic character.

1,3-cyclopentodienyl cation

I

cyclopropylium cation

II



1,3,5-cycloheptatrienyl

III

1,3-cyclobutadiene

IV

a) I

b) II

c) III

d) IV

12. The unusual stability of aromatic compounds demonstrate itself by:

a) the lower than expected heat of combustion
b) its specific chemical behavior
c) the fact that it is a cyclic compound
d) the fact that it possesses $4n+2$ π electrons

13. The reagents that will convert benzene into n-butyl benzene are:

a) n-butyl chloride, $AlCl_3$

b) n-butanol, acid

c) $CH_3\ CH_2\ CH_2\ \overset{O}{\overset{\|}{C}}—Cl$, $AlCl_3$, $Zn(H_g)$ acid

d) 1-butene, acid

14. The reagents that could be used to synthesize isopropyl benzene are:

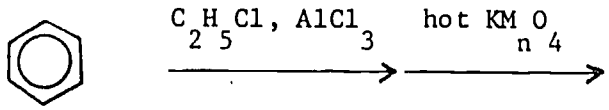
a) n-propyl chloride, BF_3

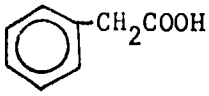
b) 2-propanol, acid

c) 2-bromopropane, $FeBr_3$

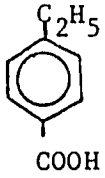
d) 1-propene, acid

15. The major product in the reaction below is:



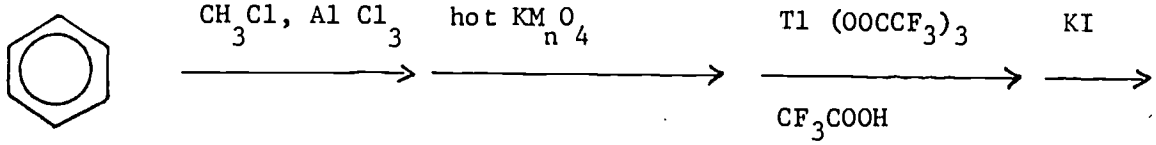
a) 

b) benzoic acid

c) 

d) ethylbenzene

16. The major product in the reaction below is:



a) benzoic acid

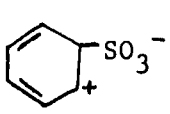
b) p-iodo benzoic acid

c) p-iodoethyl benzene

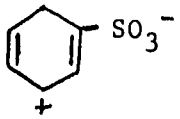
16. (continued)

d) o-iodobenzoic acid.

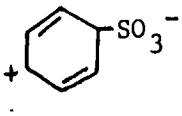
17. Select the correct resonance structures for the intermediate carbonium ion in the sulfonation reaction.



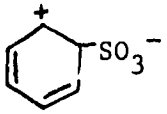
I



II



III



IV

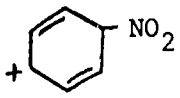
a) I

b) II

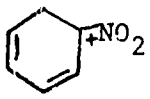
c) III

d) IV

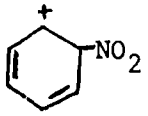
18. Select the correct resonance structures for the intermediate carbonium ion in the nitration reaction.



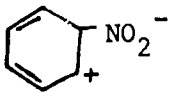
I



II



III



IV

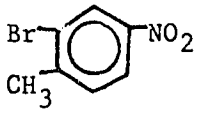
a) I

b) II

c) III

d) IV

19. The correct IUPAC name for the compound below is:



60

19. (continued)

a) 1-methyl-2-bromo-4-nitro benzene

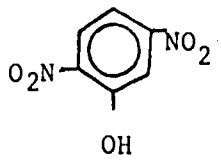
b) 1-bromo-3-nitro-6-methyl benzene

c) 3-bromo-4-methyl nitrobenzene

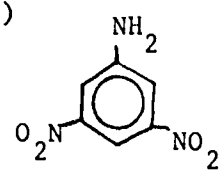
d) 2-bromo-4-nitro toluene

20. The structural formula that corresponds correctly to 2,5-dinitro-aniline is:

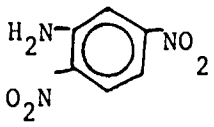
a)



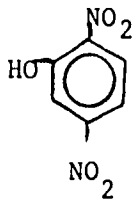
b)



c)

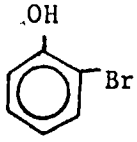


d)



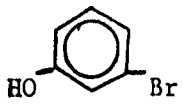
21. The structural formula that corresponds correctly to m-bromo phenol is:

a)

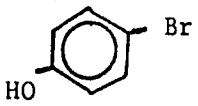


21. (continued)

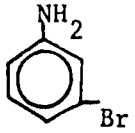
b)



c)



d)



Self Instructional Package No. 15
Form B^1 - Self Evaluation Exercise - Answers

BENZENE-AROMATICITY

1.	F	10.	b, c	19.	d
2.	T	11.	a, b, c	20.	c
3.	F	12.	c	21.	c
4.	F	13.	b, d	22.	b
5.	F	14.	b, c, d	23.	b
6.	T	15.	a, b, c	24.	c, d
7.	T	16.	b		
8.	T	17.	a, b, c, d		
9.	T	18.	b		

BENZENE - AROMATICITY

1.	T	9.	a, b, d	17.	a, c, d
2.	T	10.	c, d	18.	a, c, d
3.	T	11.	b, c	19.	d
4.	F	12.	a, b	20.	c
5.	T	13.	c	21.	b
6.	T	14.	a, b, c, d		
7.	F	15.	b		
8.	T	16.	d		